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M.M. Prange, H.H. Hooper, and J.M. Prausnitz

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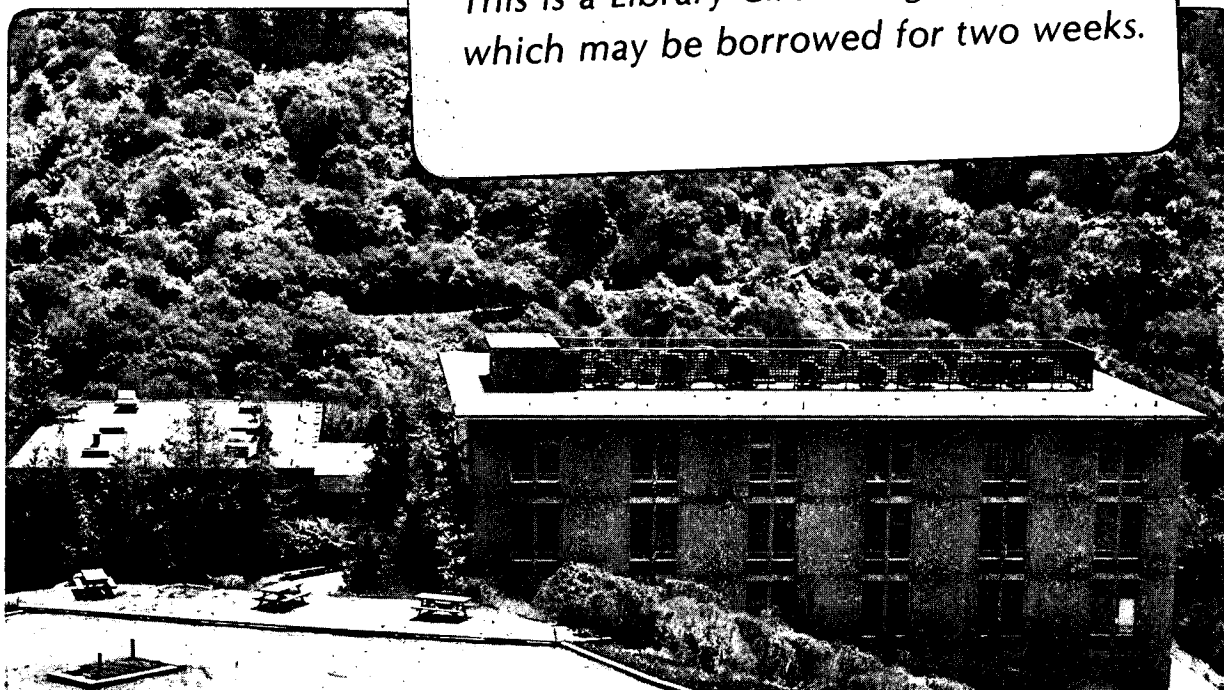
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Thermodynamics of Aqueous Systems Containing Hydrophilic Polymers or Gels

*Monika M. Prange†, Herbert H. Hooper, and John M. Prausnitz**

Chemical Engineering Department
University of California

and

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720

ABSTRACT

A quasichemical partition function is applied to represent the thermodynamic properties of aqueous solutions of nonelectrolytes, including linear polymers and crosslinked polymers (gels). The partition function extends conventional lattice theory; to take into account strong specific interactions (hydrogen bonds) as encountered in aqueous solutions, each molecule (polymer segment) may possess three energetically different types of contact sites. We distinguish between sites that interact through dispersion forces and sites which can participate in a hydrogen bond; hydrogen-bonding sites are divided into electron-pair donating sites and electron-pair accepting sites. The Helmholtz energy of the mixture is obtained using an oriented quasichemical approximation. The final equation contains three independent adjustable binary parameters; these are the exchange energies for different types of contact pairs. To represent quantitatively upper or lower critical solution phenomena, we include the semi-theoretical fluctuation correction recently proposed by de Pablo. Comparison with experimental data indicates that the proposed molecular-thermodynamic model may be useful for representing phase equilibria for a variety of aqueous systems including swelling equilibria for hydrophilic gels.

*To whom correspondence should be addressed

†present address: Hewlett-Packard, Postfach 1280, 7517 Waldbronn, West Germany

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Introduction

Water-soluble polymers are specialty chemicals used in a variety of consumer-oriented materials such as cosmetics, food additives, pharmaceuticals and personal-care products. Little is known about the thermodynamic properties of aqueous polymer solutions. This work reports some initial studies toward increasing our understanding of aqueous polymer phase behavior, and toward improving our ability to correlate that phase behavior.

Several molecular-thermodynamic models have been used to describe binary vapor-liquid equilibria and semi-dilute ternary liquid-liquid equilibria in aqueous polymer solutions (e.g. Edmond and Ogsten, 1968, Kang and Sandler, 1988, King et al., 1988). However, presently available models are not applicable to liquid-liquid equilibria for concentrated aqueous polymer solutions, especially for those solutions that exhibit a lower consolute temperature. We present here an oriented quasi-chemical model which is promising for describing such systems. We also apply this model to phase equilibria in aqueous mixtures containing hydrophilic gels. Gels are useful for drug delivery devices (e.g. Siegel, 1989; Hoffman, 1987), for separation operations in biotechnology (Freitas and Cussler, 1987), and for processing of agricultural products (Trank et al, 1988).

The thermodynamic properties of aqueous polymer solutions cannot be correlated by simple lattice models such as Flory-Huggins theory. Phase equilibria in these systems are influenced by strong, orientation-dependent interaction forces, such as hydrogen bonds. Conventional polymer-solution models (e.g. Flory, 1970, Patterson, 1969) do not take into account deviations from random mixing caused by these orientation-dependent interactions.

In recent years, several authors have proposed for polymer solutions molecular-thermodynamic models that attempt to account for nonrandom mixing. These models are often based on the local-composition concept where expressions for local composition are obtained either from essentially empirical relations (e.g. Canovas et al., 1982, Brandani, 1979, Rubio and Renuncio, 1980, Kang and Sandler, 1988) or else are derived from Guggenheim's traditional quasichemical approximation (e.g. Panayiotou, 1984, Panayiotou and Vera, 1980, Kumar, Suter and Reid, 1987). However, these models are not suitable for describing aqueous polymer systems; in particular, they are unable to

account for observed order-disorder transitions leading to lower critical solution temperatures.

To account for orientational effects, Kehiaian et al (1978), Abusleme and Vera (1985a, 1985b), and Smirnova and Victorov (1987) have proposed group-solution models. These models, however, consider the different groups to be independent of the molecule to which the groups belong. Group-contribution models, therefore, are not suitable for describing order-disorder transitions in aqueous polymer solutions.

While an upper critical solution temperature (UCST) is readily understood in terms of intermolecular forces, interpretation of a lower critical solution temperature (LCST) is more difficult (Rowlinson and Swinton, 1982). Generally, a LCST is observed when either of the following conditions prevails:

- 1) Large differences in thermal expansion of solvent and solute. This situation is often encountered in polymer/volatile-solvent systems [e.g. poly(styrene)/acetone (Siow et al., 1972, Zeman and Patterson, 1972)] when the system temperature approaches the critical temperature of the solvent. As temperature rises, the solvent expands more rapidly than the solute; solubility decreases until two separate phases are formed. This behavior is well described by free-volume theories [e.g. Flory, 1970, Patterson, 1969, Lacombe and Sanchez, 1976, Sanchez and Lacombe, 1978].
- 2) Order-disorder transitions, as encountered in systems of molecules capable of forming hydrogen bonds, e.g. water/nicotine (Cambell et al., 1958) and water/poly(ethyleneglycol) (Malcolm and Rowlinson, 1957). More than fifty years ago, Hirschfelder et al. (1937) suggested a qualitative physical picture to explain the occurrence of LCSTs in hydrogen-bonding systems: at temperatures below the LCST, mutual solubility is due to highly orientation-dependent interactions (hydrogen bonds) between unlike species. As the temperature rises, molecular rotation increases, causing hydrogen bonds to break. If dispersion-force interactions between unlike species are weaker than those between like species, the system splits into two phases.

In this paper we are concerned with aqueous solutions at ordinary temperatures; therefore the free-volume theories are not useful here.

Models that attempt to incorporate order-disorder transitions were proposed in the early 1950's by Barker (Barker, 1952, Barker and Fock, 1953) and Tompa (1953). Barker and Fock considered a lattice with coordination number z where each site is occupied by one molecule of either species 1 or 2. One or more of the z contact points of each molecule were taken to be energetically different from the others. Barker and Fock developed this model with the quasichemical approximation and were able to show that, in principle, this model was capable of predicting LCSTs and UCSTs for suitable choices of interaction parameters. However, Barker and Fock were not able to reproduce liquid-liquid equilibria quantitatively. Further, their model is restricted to solutions of equal-sized molecules and therefore it is not directly applicable to aqueous polymer solutions.

Sjoeberg and Karlstroem (1988) have presented a model for ternary aqueous systems. As temperature rises, the authors assume a change of polymer conformation from a hydrophilic to a hydrophobic state.

To describe binary systems of nearly equal-sized molecules with oriented interactions, decorated lattice models have been proposed that are "exactly soluble" in the sense that they can be mapped onto a three-dimensional Ising model for which known solutions exist (e.g. Andersen and Wheeler, 1978, Wheeler, 1975). The mathematical complexity of these models makes extension to polymer solutions and multicomponent systems difficult.

We describe here a theory which, in spirit, is similar to that of Barker and Fock; our goal is to interpret and quantitatively correlate phase equilibria in aqueous polymer solutions. Our partition function is formally similar to that of Abusleme and Vera (1985a), as discussed near the end of the next section.

Lattice Theory for a Mixture of Hydrogen-Bonded Liquids

Figure 1 shows a two-dimensional representation of our lattice model. The coordination number of the lattice is z (usually taken to be 10). Each molecule possesses zq contact sites through which it can interact with nearest neighbors. For linear or branched-chain molecules, zq is related to r , the number of segments per molecule, by

$$zq = r(z - 2) + 2 \quad (1)$$

To account for hydrogen bonding, we stipulate that the contact sites (or surface regions) of a molecule (polymer segment) can exhibit different potential energies. Each molecule (segment) of species i can possess three types of contact sites: hydrogen-bond donating sites, hydrogen-bond accepting sites, and sites which interact through dispersion forces. (Here we define electron-pair acceptors as hydrogen-bond donating sites, and electron-pair donors as hydrogen-bond accepting sites). We use z_i^α and z_i^β , respectively, to denote the number of hydrogen-bond-donating and hydrogen-bond-accepting sites per segment of molecule i . The remaining contacts, $z_i^D (= z - z_i^\alpha - z_i^\beta)$, interact through dispersion forces.

For a given molecule, z_i^α and z_i^β are determined from molecular structure. Water, for example, can participate in two hydrogen bonds as a donor ($z_i^\alpha = 2$), and in two hydrogen bonds as an acceptor ($z_i^\beta = 2$). Some organic compounds can participate in hydrogen bonds only as donors ($z_i^\beta = 0$), or only as acceptors ($z_i^\alpha = 0$); examples include chloroform and (neglecting end-groups) polyethylene glycol.

For a binary system in which each component contains α , β , and D sites, there are twenty-one different types of contact pairs, N_{kl} . Here, k and l are contact-site indices, with a different index for α , β , and D sites on each molecule i . In the simplest case, where the interaction energies u_{kl} between all contact pairs are identical, all molecules (resp. contact sites) are randomly distributed over the lattice. The numbers of different kl pairs are then given by the overall probability that two contact sites of a given type are nearest neighbors. These numbers are readily calculated from the overall composition and the number of different contact sites per molecule (segment). Guggenheim calls this simple case the zeroth approximation (Guggenheim, 1952).

For those cases where molecules have homogeneous surface potentials (i.e., we do not distinguish between different types of contacts) but where $u_{ij} \neq u_{ii} \neq u_{jj}$, we can also calculate the number of ij contact pairs using Guggenheim's traditional quasichemical approximation. We then obtain

modest deviations from random mixing. Guggenheim calls this case the first approximation.

However, for systems in which strong specific interactions are significantly different from weak interactions, we expect large deviations from random mixing. To take these large deviations into account, we write the partition function Q for a hydrogen-bonding fluid in the form

$$Q = Q_{comb,random} Q_{comb,nonrandom} Q_E Q_{vib,rot} \quad (2)$$

where

$Q_{comb,random}$ = random contribution to combinatorial factor,

depending only on number of molecules and molecular size

$Q_{comb,nonrandom}$ = nonrandom contribution to combinatorial factor, depending primarily on the interaction energies between different types of pairs relative to thermal energy kT , where k is Boltzmann's constant

Q_E = energetic contribution to the partition function

$Q_{vib,rot}$ = contributions to the partition function from molecular vibrations and rotations.

To obtain an expression for the Gibbs energy of mixing from the partition function, we assume that at the pressures and temperatures of interest here, the change in molar volume upon mixing is negligible:

$$[\Delta G_{mixing}]_{T,P} \approx [\Delta A_{mixing}]_{T,V} = -kT \ln Q_{mixing} \quad (3)$$

where A is the Helmholtz energy.

The chemical potential per molecule of component i is calculated from the partition function according to

$$\Delta\mu_i = \mu_i - \mu_i^o = \frac{\partial(G_{mixture} - G_i^o)}{\partial N_i} \approx -kT \frac{\partial \ln Q_{mixing}}{\partial N_i} \quad (4)$$

where N_i is the number of molecules of species i . The differentiation in Equation (4) is at constant temperature, constant pressure and constant N_j .

Superscript $^{\circ}$ refers to the standard state, here chosen to be that of the pure component at system temperature and pressure. Q_{mixing} is given by

$$Q_{mixing} = Q_{mixture} / \prod_i Q_{pure\ i} \quad (5)$$

Following Guggenheim (1952), we assume that the vibrational and rotational contributions to the partition function do not change significantly upon mixing; therefore the $Q_{vib,rot}$ terms cancel out in Equation (5).

For the random contribution to the combinatorial factor we use an expression given by Guggenheim (1944a). In the derivation of this combinatorial factor, the relation between r and q is given by Equation (1) which holds only for linear or branched-chain molecules. As discussed later, to calculate swelling equilibria in systems containing crosslinked polymers, we use for Q_{random} the Flory-Huggins combinatorial term. Both random combinatorial terms are functions only of the numbers and sizes of the molecules in the mixture.

To obtain an expression for the non-random combinatorial term, we use an oriented quasichemical approximation which is an extension of the quasichemical approximation suggested by Guggenheim (1944b). This extension follows from distinguishing between sites denoted by α , β , and D as outlined below.

The energy contribution to the partition function is given by

$$Q_E = \exp - (E_{latt} / kT) \quad (6)$$

For the lattice energy E_{latt} we assume pairwise additivity of interaction energies.

To calculate $Q_{nonrandom}$ and Q_E , it is necessary to evaluate the numbers of different contact pairs as a function of composition, temperature and the interaction energies between contacts. As suggested by Panayiotou and Vera (1980), we express the numbers of nonrandom contact pairs in terms of nonrandom factors Γ such that in a system containing m components, for a given pair

$$N_{ij}^{\alpha\beta} = (N_{ij}^{\alpha\beta})_r \Gamma_{ij}^{\alpha\beta} \quad (i = 1, m; j = 1, m) \quad (7a)$$

$$N_{ij}^{\alpha D} = (N_{ij}^{\alpha D})_r \Gamma_{ij}^{\alpha D} \quad (i = 1, m; j = 1, m) \quad (7b)$$

$$N_{ij}^{\beta D} = (N_{ij}^{\beta D})_r \Gamma_{ij}^{\beta D} \quad (i = 1, m; j = 1, m) \quad (7c)$$

$$N_{ij}^{\alpha \alpha} = (N_{ij}^{\alpha \alpha})_r \Gamma_{ij}^{\alpha \alpha} \quad (i = 1, m; j = 1, m) \quad (7d)$$

$$N_{ij}^{\beta \beta} = (N_{ij}^{\beta \beta})_r \Gamma_{ij}^{\beta \beta} \quad (i = 1, m; j = 1, m) \quad (7e)$$

$$N_{ij}^{D D} = (N_{ij}^{D D})_r \Gamma_{ij}^{D D} \quad (i = 1, m; j = 1, m) \quad (7f)$$

where subscript r denotes random mixing. The nonrandom factors Γ are evaluated from minimization of the Helmholtz energy, with constraints from contact-site balances. We then obtain quasichemical equations of the form

$$\frac{[\Gamma_{ij}^{\alpha \beta}]^2}{[\Gamma_{ii}^{\alpha \alpha}] [\Gamma_{jj}^{\beta \beta}]} = \exp - \left[2 \omega_{ij}^{\alpha \beta} / kT \right] \quad (i = 1, m; j = 1, m) \quad (8a)$$

$$\frac{[\Gamma_{ij}^{\alpha D}]^2}{[\Gamma_{ii}^{\alpha \alpha}] [\Gamma_{jj}^{D D}]} = \exp - \left[2 \omega_{ij}^{\alpha D} / kT \right] \quad (i = 1, m; j = 1, m) \quad (8b)$$

$$\frac{[\Gamma_{ij}^{\beta D}]^2}{[\Gamma_{ii}^{\beta \beta}] [\Gamma_{jj}^{D D}]} = \exp - \left[2 \omega_{ij}^{\beta D} / kT \right] \quad (i = 1, m; j = 1, m) \quad (8c)$$

$$\frac{[\Gamma_{ij}^{\alpha \alpha}]^2}{[\Gamma_{ii}^{\alpha \alpha}] [\Gamma_{jj}^{\alpha \alpha}]} = \exp - \left[2 \omega_{ij}^{\alpha \alpha} / kT \right] \quad (i = 1, m; j = 1, m; i \neq j) \quad (8d)$$

$$\frac{[\Gamma_{ij}^{\beta \beta}]^2}{[\Gamma_{ii}^{\beta \beta}] [\Gamma_{jj}^{\beta \beta}]} = \exp - \left[2 \omega_{ij}^{\beta \beta} / kT \right] \quad (i = 1, m; j = 1, m; i \neq j) \quad (8e)$$

$$\frac{[\Gamma_{ij}^{D D}]^2}{[\Gamma_{ii}^{D D}] [\Gamma_{jj}^{D D}]} = \exp - \left[2 \omega_{ij}^{D D} / kT \right] \quad (i = 1, m; j = 1, m; i \neq j) \quad (8f)$$

where the exchange energies ω are given by

$$\omega_{ij}^{\alpha \beta} = u_{ij}^{\alpha \beta} - \frac{1}{2} u_{ii}^{\alpha \alpha} - \frac{1}{2} u_{jj}^{\beta \beta} \quad (i = 1, m; j = 1, m) \quad (9a)$$

$$\omega_{ij}^{\alpha D} = u_{ij}^{\alpha D} - \frac{1}{2} u_{ii}^{\alpha \alpha} - \frac{1}{2} u_{jj}^{D D} \quad (i = 1, m; j = 1, m) \quad (9b)$$

$$\omega_{ij}^{\beta D} = u_{ij}^{\beta D} - \frac{1}{2} u_{ii}^{\beta \beta} - \frac{1}{2} u_{jj}^{D D} \quad (i = 1, m; j = 1, m) \quad (9c)$$

$$\omega_{ij}^{\alpha \alpha} = u_{ij}^{\alpha \alpha} - \frac{1}{2} u_{ii}^{\alpha \alpha} - \frac{1}{2} u_{jj}^{\alpha \alpha} \quad (i = 1, m; j = 1, m; i \neq j) \quad (9d)$$

$$\omega_{ij}^{\beta \beta} = u_{ij}^{\beta \beta} - \frac{1}{2} u_{ii}^{\beta \beta} - \frac{1}{2} u_{jj}^{\beta \beta} \quad (i = 1, m; j = 1, m; i \neq j) \quad (9e)$$

$$\omega_{ij}^{D D} = u_{ij}^{D D} - \frac{1}{2} u_{ii}^{D D} - \frac{1}{2} u_{jj}^{D D} \quad (i = 1, m; j = 1, m; i \neq j) \quad (9f)$$

The contact-site balance equations in a system of m components can be written as

$$\Gamma_{ii}^{\alpha \alpha} = \frac{1 - \left[\sum_j \theta_j^{\alpha} \Gamma_{ij}^{\alpha \alpha} + \sum_j \theta_j^{\beta} \Gamma_{ij}^{\alpha \beta} + \sum_j \theta_j^D \Gamma_{ij}^{\alpha D} + \theta_i^{\beta} \Gamma_{ii}^{\alpha \beta} + \theta_i^D \Gamma_{ii}^{\alpha D} \right]}{\theta_i^{\alpha}} \quad (10a)$$

$$\Gamma_{ii}^{\beta \beta} = \frac{1 - \left[\sum_j \theta_j^{\alpha} \Gamma_{ij}^{\beta \alpha} + \sum_j \theta_j^{\beta} \Gamma_{ij}^{\beta \beta} + \sum_j \theta_j^D \Gamma_{ij}^{\beta D} + \theta_i^{\alpha} \Gamma_{ii}^{\beta \alpha} + \theta_i^D \Gamma_{ii}^{\beta D} \right]}{\theta_i^{\beta}} \quad (10b)$$

$$\Gamma_{ii}^{D D} = \frac{1 - \left[\sum_j \theta_j^{\alpha} \Gamma_{ij}^{D \alpha} + \sum_j \theta_j^{\beta} \Gamma_{ij}^{D \beta} + \sum_j \theta_j^D \Gamma_{ij}^{D D} + \theta_i^{\alpha} \Gamma_{ii}^{D \alpha} + \theta_i^{\beta} \Gamma_{ii}^{D \beta} \right]}{\theta_i^D} \quad (10c)$$

where: $i = 1, m; j = 1, m; j \neq i$

Here θ_i^{α} , θ_i^{β} , and θ_i^D are contact-site fractions, defined by

$$\theta_i^{\alpha} \equiv \frac{z_i^{\alpha} q_i N_i}{N z q} ; \quad \theta_i^{\beta} \equiv \frac{z_i^{\beta} q_i N_i}{N z q} ; \quad \theta_i^D \equiv \frac{z_i^D q_i N_i}{N z q} \quad (11)$$

with $N z q = z \sum_i q_i N_i$

Details leading to Equation (8) and Equation (10) are given as supplementary material.

To describe a binary system, we require twenty one nonrandom factors Γ . To obtain them, we have fifteen quasichemical equations (four equations each of types 8a, 8b, and 8c, and one equation each of types 8d, 8e, and 8f) in addition to six contact-site balance equations (two equations each of

types 10a, 10b, and 10c).

For solutions of linear or branched polymers, we obtain for the chemical potential per mole of component i

$$\Delta\mu_i = -RT \left[r_i (\frac{1}{2}z - 1) \ln \phi_i - \frac{1}{2}z q_i \ln \theta_i - 1 + \frac{\phi_i}{x_i} + \frac{1}{2}z q_i (1 - \frac{\phi_i}{\theta_i}) + \right. \quad (12)$$

$$\left. \frac{1}{2}z_i^\alpha q_i \ln \frac{[\Gamma_{ii}^{\alpha\alpha}]_{\text{pure}}}{[\Gamma_{ii}^{\alpha\alpha}]_{\text{mix}}} + \frac{1}{2}z_i^\beta q_i \ln \frac{[\Gamma_{ii}^{\beta\beta}]_{\text{pure}}}{[\Gamma_{ii}^{\beta\beta}]_{\text{mix}}} + \frac{1}{2}z_i^D q_i \ln \frac{[\Gamma_{ii}^{DD}]_{\text{pure}}}{[\Gamma_{ii}^{DD}]_{\text{mix}}} \right]$$

where ϕ is the volume fraction: $\phi_i = \frac{N_i r_i}{\sum_j N_j r_j}$

and θ is the surface fraction: $\theta_i = \frac{N_i q_i}{\sum_j N_j q_j}$

The first five terms of the right-hand side of Equation (12) give contributions from random mixing; the last three terms give the non-randomness contribution and the energetic contribution.

If we do not allow for hydrogen-bonding contacts, then z_i^α and z_i^β become equal to zero and the nonrandom factors for the pure components Γ_{ii} are equal to unity. In that event our model reduces to the first approximation suggested by Guggenheim (1952). If we equate interaction energies between all contact pairs (i.e., if we set all exchange energies to zero), then the nonrandom factors are unity for the pure components and for the mixture, and the last three terms of Equation (12) are equal to zero. In that case, our model reduces to Guggenheim's zeroth approximation (Guggenheim, 1952).

The similarity of our partition function to that of Abusleme and Vera (1985a) becomes apparent if we regard our model as a group-contribution model that contains three groups (α , β , and D). However, unlike Abusleme and Vera, we assume different interaction potentials for the same group, depending on whether it belongs to molecule A or molecule B. Thus, while our final equations are similar to those of Abusleme and Vera, our physical picture leading to these equations is significantly different.

Details of the derivation of the partition function and the expression for the chemical potential are available as supplementary material.

Comparison with Experimental Data

To calculate phase equilibria, the chemical potential of every component in the mixture must be evaluated as a function of temperature, composition and interaction energies. Structural parameters r_i , q_i , z_i^α , and z_i^β are obtained from molecular size (number of structural units per molecule) and from molecular structure (e.g., number of possible hydrogen bonds per structural unit). For water we use $r = 1$, $q = 1$, $z^\alpha = 2$, and $z^\beta = 2$.

The exchange energies are adjustable binary parameters. For a binary system in which both components contain α , β , and D contact sites, there are fifteen different exchange energies. To make tractable the number of adjustable parameters, we group exchange energies into four categories, and make a reasonable simplifying assumption for each of the first three. The four groups (and the simplifying assumptions) are as follows:

(1) energies of hydrogen bonding between like molecules: $\omega_{11}^{\alpha\beta} = \omega_{22}^{\alpha\beta}$

(2) energies of hydrogen bonding between unlike molecules: $\omega_{12}^{\alpha\beta} = \omega_{21}^{\alpha\beta}$

(3) weak attractions between hydrogen bonding and non-hydrogen bonding contacts:

$$\omega_{11}^{\alpha D} = \omega_{11}^{\beta D} = \omega_{22}^{\alpha D} = \omega_{22}^{\beta D} = \omega_{12}^{\alpha D} = \omega_{12}^{\beta D} = \omega_{21}^{\alpha D} = \omega_{21}^{\beta D}$$

(4) weak attractions between unlike molecules: ω_{12}^{DD}

Exchange energies of types (1) and (2) are always negative, reflecting the favorable energetics of hydrogen-bond formation. Exchange energies of type (4) are typically positive, indicating that van der Waals interactions are less favorable between unlike molecules than between like molecules. Finally, exchange energies of type (3) are negative due to the unfavorable energetics of α - α and β - β contacts, relative to α - D and β - D contacts.

Two exchange energies have been omitted from the above discussion: $\omega_{12}^{\alpha\alpha}$ and $\omega_{12}^{\beta\beta}$. Interaction potentials for α - α and β - β contacts between unlike molecules are not likely to be significantly different from those between like molecules. Thus, $\omega_{12}^{\alpha\alpha}$ and $\omega_{12}^{\beta\beta}$ are set to zero in all cases.

A final simplification is to fix the value of the pure-component hydrogen-bonding exchange energies ($\omega_{11}^{\alpha\beta}$ and $\omega_{22}^{\alpha\beta}$) at a constant (negative) value for all systems. From experience with data reduction, we find that good quantitative representation of experimental data is obtained when

$$\omega_{11}^{\alpha\beta} / k = \omega_{22}^{\alpha\beta} / k = -200.0 \text{ K}$$

and when the remaining parameters are adjusted. Thus, in a binary system, we have three adjustable exchange-energy parameters: $\omega_{12}^{\alpha\beta}$ ($= \omega_{21}^{\alpha\beta}$), $\omega_{12}^{D,D}$, and ω^D . The parameter ω^D refers to exchange energies of type (3), where $*$ = α or β , and the exchange energy is identical for 1-1, 2-2, 1-2, and 2-1 contacts.

The simplifications made here reduce to three the number of adjustable parameters in the model without sacrificing the physical picture used in deriving the partition function. While these simplifications may appear extreme, it is important to remember that energy parameters used to correlate experimental data are relative, not absolute representations of underlying molecular interactions (see recent computer simulation studies of Madden et al, 1989). Thus, while we have fixed the values of $\omega_{11}^{\alpha\beta}$ and $\omega_{22}^{\alpha\beta}$, the remaining parameters indicate the relative magnitudes (and signs) of other interactions with respect to these fixed values.

When compared to computer calculations, Madden found that Guggenheim's quasichemical theory agrees fairly well with simulation over a wide concentration range; the other lattice models Madden considered agreed less favorably with simulation. Madden's work thus lends support to our choice of quasichemical theory as a framework for developing an oriented lattice model.

In the following sections, we apply the oriented quasichemical model to vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) for several aqueous solutions containing molecules of different sizes.

Vapor-Liquid Equilibria (VLE)

Figure 2 shows vapor-liquid equilibria for aqueous solutions of poly(ethyleneglycol) (PEG) and poly(propyleneglycol) (PPG) (Malcolm and Rowlinson, 1957). The activity of the solvent is plotted as a function of volume fraction of the polymer for PEG solutions of different molecular weights. The solvent-activity data for the low molecular-weight (300) PEG differ appreciably from those for the higher molecular-weight fractions. This difference is probably due to the terminal -OH groups which have considerable influence on the behavior of the low molecular-weight fractions. Because we neglected end groups in determining z_2^{α} and z_2^{β} for PEG, it was necessary to allow one binary parameter, $\omega_{12}^{\alpha\beta}$, to differ for the low and high molecular-weight fractions. Table 1 gives parameters used to fit VLE data.

Figure 2 shows that the model can represent the data within experimental error. However, such fitting is not remarkable. Other, simpler Gibbs-energy models also fit these VLE data. It is much more difficult to fit binary liquid-liquid equilibrium data.

Liquid-Liquid Equilibria (LLE)

Figures 3 and 4 show experimental and calculated LLE for aqueous systems containing molecules ranging in molecular weight between 56 (propenal) and 290,000 poly(N-isopropylacrylamide). Table 2 gives parameters used to correlate LLE.

The systems phenol/water and propenal/water exhibit upper critical solution temperatures. However, PEG/water, PPG/water and poly(N-isopropylacrylamide)/water exhibit lower critical solution temperatures. These LCSTs are caused by order-disorder transitions due to the breakage of hydrogen bonds with increasing temperature. While conventional polymer-solution models can predict the existence of UCSTs, they cannot predict the existence of LCSTs that are caused by order-disorder transitions, unless we assign unreasonable temperature dependences to the energy parameters. The broken lines in Figures 3 and 4 show coexistence curves calculated from our model. Without modification, the oriented quasichemical model is able to reproduce qualitatively upper as well as lower critical solution temperatures with temperature-independent parameters. In all systems

we observe that, remote from the critical point, agreement between experimental and calculated results is good; however, as the critical point is approached, deviations become unacceptably large.

These deviations are caused by two effects:

a) For simplicity, we have here assumed that the exchange energies are temperature independent. This assumption neglects the effect of lattice expansion and, more important, it neglects changes in rotational and vibrational partition functions due to mixing.

b) The oriented quasichemical model is classical in the sense that it does not take into account fluctuations of compositions around mean equilibrium values. Near the critical point of a system, these fluctuations become important and, very close to the critical point, they determine the properties of the system (Sengers and Levelt Sengers, 1978).

De Pablo and Prausnitz (1988) have developed a semi-theoretical correction to take these fluctuations into account. Along the coexistence curve, the excess Gibbs energy can be expressed as

$$G^E = G_{conv}^E F \quad (13)$$

where G_{conv}^E is the excess Gibbs energy calculated from a "conventional" model (such as ours) and where F is a decay function that describes the effect of fluctuations as a function of distance from the critical point. For a binary system, along the coexistence curve, F is only a function of temperature. As suggested by de Pablo, F is given by

$$F = 1 - K \exp a \left[\left(\frac{T_c - T}{T_c} \right)^2 \right]^b \quad (14)$$

where T_c is the critical temperature of the system. At the critical point, $F = 1 - K$ and therefore K can be calculated from stability criteria. Constants a and b are not adjustable parameters; they are determined from known exponents in scaling laws, as discussed by de Pablo and Prausnitz (1988). Constant a is always negative and constant b is always positive.

The solid lines in Figures 3 and 4 show that, by introducing de Pablo's correction into our model, a much better representation of the data can be achieved. It is important to note that parameters K , a and b are not adjustable binary parameters. They are determined only from theoretical

criteria and from the experimental coordinates of the critical point.

Swelling Equilibria for Hydrophilic Gels

Gels are crosslinked-polymer networks that can absorb solvent but are insoluble in the solvent. The equilibrium solvent content of the gel depends upon temperature, polymer-solvent interaction and the elastic forces in the network that counteract swelling. It has been observed that with changing temperature, some gels can undergo phase transitions from a highly swollen (high solvent content) state to a collapsed (low solvent content) state (Tanaka, 1978; Hirokawa and Tanaka, 1984; Hoffman, 1987; Freitas and Cussler, 1987). Gels of polymers that exhibit an UCST are collapsed at low temperatures and swell as the temperature rises. Gels of polymers that exhibit a LCST show the inverted behavior; they are swollen at low temperatures and collapse as the temperature rises. We have applied the oriented quasichemical theory to describe swelling equilibria in the system water/poly(N-isopropylacrylamide).

Since the chemical potential given by Equation (12) is valid only for mixtures of linear or branched molecules, we must use another expression for the random contribution to the combinatorial factor. Further, in a crosslinked polymer, elastic forces in the polymer network counteract swelling; these forces contribute to the Gibbs energy. According to Flory (1953), the chemical potential of a solvent in a gel phase coexisting with pure solvent is given by

$$\mu_1 - \mu_1^0 = \Delta\mu_1 = \Delta\mu_{1,mixing} + \Delta\mu_{1,elastic} \quad (15)$$

We use the Flory-Huggins combinatorial term for the random contribution to $\Delta\mu_{1,mixing}$. The nonrandom and energetic contributions to the partition function are the same as those described above for systems containing non-crosslinked polymers. In a system containing a crosslinked-polymer network, the number of polymer molecules (not the number of segments) approaches zero (Flory, 1953). In this limit we obtain

$$\Delta\mu_{1,mixing} = -RT \left[\ln \phi_1 + \phi_2 + \frac{1}{2} z_1^\alpha q_1 \ln \frac{[\Gamma_{11}^{\alpha\alpha}]_{pure}}{[\Gamma_{11}^{\alpha\alpha}]_{mix}} + \frac{1}{2} z_1^\beta q_1 \ln \frac{[\Gamma_{11}^{\beta\beta}]_{pure}}{[\Gamma_{11}^{\beta\beta}]_{mix}} + \frac{1}{2} z_1^D q_1 \ln \frac{[\Gamma_{11}^{DD}]_{pure}}{[\Gamma_{11}^{DD}]_{mix}} \right] \quad (16)$$

where ϕ_1 is the volume fraction of the solvent and ϕ_2 is the volume fraction of the gel in the gel phase. An expression for the contribution of elastic forces to the chemical potential can be obtained from the theory of rubber elasticity. We use an expression given by Flory (1953),

$$\Delta\mu_{1,elastic} = RT \left[\frac{v_1}{v_u} \phi_2^\circ (\rho - \rho_t) \left[\left(\frac{\phi_2}{\phi_2^\circ} \right)^{\frac{1}{3}} - \frac{\phi_2}{2\phi_2^\circ} \right] \right] \quad (17)$$

where

v_1 = molar volume of solvent

v_u = molar volume of monomer unit

ϕ_2° = volume fraction of the gel in the standard state (i.e. the volume fraction of the gel in the state at which it is prepared)

ρ = fraction of monomer units that are connected via crosslinks

ρ_t = fraction of chains in the network that are terminated by a crosslink only on one end. These chains do not contribute to elasticity.

Appendix I gives details concerning calculation of swelling equilibria.

Figure 5 shows experimental and calculated swelling equilibria for the system water/poly(N-isopropylacrylamide) gel (Freitas, 1987) which shows an inverted phase transition; the ratio of volume of gel in equilibrium with water (V) to that of dry gel (V_o) is plotted against temperature. The calculated curve is obtained using Equations (15)-(17) and using the procedure outlined in Appendix I. The gel composition parameters required in Equation (17) are obtained from conditions under which the gel is prepared ($\rho = 0.018$, $\phi_2^\circ = 0.07$); the value of ρ_t is estimated to be 0.0001. For the exchange energies, we use the parameters obtained from correlating LLE for the uncrosslinked poly(N-isopropylacrylamide)/water system (Table 2). Thus, the calculated curve shown in Figure 5 has *not* been fit to the experimental swelling data; this curve is a prediction based

on the known gel composition at preparation, and on independently-obtained exchange-energy parameters.

The semi-quantitative agreement of the predicted swelling equilibria with experiment is encouraging. The predicted gel-collapse temperature is approximately three degrees lower than the observed collapse temperature. This is not surprising, however, considering that the calculated critical temperature for the uncrosslinked system is also too low when using the uncorrected version of our model. If the exchange energies were correlated to the experimental swelling data, the collapse temperature would be more accurately reproduced.

The calculations predict higher degrees of swelling at low temperatures than those observed experimentally. This disagreement is probably due to the expression we have used to describe the elastic effects on swelling. Equation (17) assumes that the chains in the gel network are distributed in a Gaussian manner about their average chain lengths. While this assumption is reasonable for short chain extensions, it introduces significant errors at high degrees of swelling. A large body of information exists on rubber elasticity (Mark and Erman, 1988; Erman and Flory, 1986; Treloar, 1958), and more accurate expressions for the elastic contribution to the Gibbs energy of swelling are available. We used Equation (17) because its simplicity was consistent with our goal to demonstrate the applicability of the oriented quasichemical model for describing gel swelling equilibria.

Conclusions

We have used an oriented quasichemical model to correlate phase equilibria for aqueous solutions of hydrophilic polymers and gels. By distinguishing between hydrogen-bonding and dispersion-force interactions, and without using temperature-dependent parameters, the model can predict the existence of lower critical solution temperatures that are caused by order-disorder transitions.

We have used the oriented quasichemical model to correlate VLE and LLE for aqueous systems containing small and large hydrogen-bonding solutes. Satisfactory representation is obtained for VLE and LLE in systems showing upper and lower critical solution temperatures. To represent quantitatively LLE near an upper or lower consolute point, we add to the model dePablo's fluctuation

correction for the coexistence curve.

Encouraging results were obtained by applying the model to swelling equilibria for a gel/water system. Using energy parameters optimized to LLE data for the uncrosslinked poly(N-isopropylacrylamide)/water system, the model predicts swelling equilibria (and gel collapse) in semi-quantitative agreement with experiment. Quantitative representation of swelling data will require a more realistic expression for the elastic contribution to the Gibbs energy.

Finally, it is important to note that all of the exchange energy parameters obtained from regressing experimental data have magnitudes and signs consistent with the physical premise of our model. The model appears to represent correctly the competition between hydrogen-bonding and dispersion-force interactions which leads to order-disorder transitions and lower critical solution behavior. These conclusions regarding parameter significance are necessarily qualitative in light of recent computer simulation studies (Madden et al, 1989). However, the (relatively) favorable comparison of quasichemical theory with simulation (Madden et al, 1989) lends support to these conclusions and to the simplifying assumptions made in applying our model to real systems.

Acknowledgments

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List of symbols used

a = constant in de Pablo's function

A = Helmholtz energy

b = constant in de Pablo's function

E_{latt} = lattice energy

G = Gibbs energy

G^E = excess Gibbs energy

k = Boltzmann constant

K = constant in de Pablo's function

N_i = number of molecules of type i

$N_{ij}^{\alpha\beta}$ = number of $_{ij}^{\alpha\beta}$ contacts

m = number of components in a mixture

n_i = number of moles of component i

P = pressure

q = surface parameter

Q = partition function

r = size parameter

R = gas constant

T = temperature

$u_{ij}^{\alpha\beta}$ = interaction energy of $_{ij}^{\alpha\beta}$ contact

V = volume

v_1 = molar volume of solvent

v_u = molar volume of monomer unit

z_i^α = number of α sites per segment of component i

z_i^β = number of β sites per segment of component i

z = coordination number

Greek letters

$\Gamma_{ij}^{\alpha\beta}$ = nonrandom factor for $\alpha\beta$ contact

θ_i = surface fraction of component i

θ_i^α = contact-site fraction for α sites on component i

θ_i^β = contact-site fraction for β sites on component i

θ_i^D = contact-site fraction for D sites on component i

μ_i = chemical potential of component i

ρ = crosslink density (fraction of monomer units engaged in a crosslink)

ρ_t = fraction of terminated polymer chains

ϕ_i = volume fraction of component i

$\omega_{ij}^{\alpha\beta}$ = exchange energy for a $\alpha\beta$ contact

Superscripts

o = standard state

$^\alpha$ = hydrogen-bond donating site

$^\beta$ = hydrogen-bond accepting site

D = dispersion-force interaction site

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Appendix I

Calculation of swelling equilibria in solvent/gel systems

In an isothermal and isobaric system containing a crosslinked polymer in equilibrium with pure solvent, swelling equilibria must fulfill the equilibrium condition

$$\mu_1' = \mu_1'' \quad (\text{A-1})$$

where ' and '' denote the pure solvent phase and the gel phase, respectively; subscript 1 refers to the solvent.

As the gel phase is in equilibrium with pure solvent, we can rewrite the equilibrium condition

$$\mu_1'' - \mu_1^{\circ} = \Delta\mu_1'' = 0 \quad (\text{A-2})$$

Here superscript $^{\circ}$ refers to the standard state which is the pure liquid at system temperature and pressure.

Figure A-1 shows solvent chemical-potential isotherms for a gel/solvent system which exhibits a LCST, plotted versus composition of the gel phase. A distinguishing feature of phase equilibria for crosslinked polymers (gels) is an unstable region ($\partial\mu_1/\partial\phi_1 < 0$) at high concentration of solvent in the gel-phase (high degree of swelling). This instability is caused by contributions of elastic forces to the chemical potential of the solvent which prevent the polymer from becoming completely soluble.

Figure A-2 shows the coexistence and spinodal curves for the gel/solvent system. These curves can be obtained from the isotherms in Figure A-1 by applying stability criteria and equilibrium conditions. The equilibrium composition of the gel phase is found from the solution of Equation (A-2). At temperatures remote from the transition temperature T_i , Equation (A-2) has only one root; only one gel phase can coexist with the pure solvent. Between T_c and T_s , however, we encounter a region where two gel phases can coexist with the solvent; T_s is the temperature at which the spinodal curve

shows an extremum on the solvent-rich side (see Figure A-2). Above this temperature only one gel phase can coexist with the solvent. Coexistence of two gel phases in equilibrium with pure solvent is only encountered in gels of those linear polymers that show partial miscibility with the solvent.

The binodal curve for the coexistence of the two gel phases can be determined by applying the Maxwell condition to the chemical potential isotherms; in a solvent/gel system this condition is given by

$$\int_{\text{gel phase } S}^{\text{gel phase } C} \phi_1 d\Delta\mu_1'' = 0 \quad (\text{A-3})$$

Here S and C denote respectively the swollen and the collapsed gel phases.

A general derivation of the Maxwell condition in a binary system is given in Table A-1, augmented by Figure A-3.

Points along the binodal curve are represented by squares in Figures A-1 and A-2. The triangles indicate points on the spinodal curve which represents the limit of stability. For a given pressure, the phase transition temperature is that temperature for which Equations (A-2) and (A-3) are satisfied. As the pressure changes, the phase transition can be shifted along the binodal curve until at some critical pressure, T_i and T_c coincide and the phase transition becomes continuous (Hirotsu, 1988, Lee et al, 1989). The critical point in a gel is analogous to the critical point of a pure solvent in the sense that at T_c discontinuous phase transitions become continuous.

Table 1 :

Parameters for VLE calculations in aqueous systems

Solute (2)	r_2	q_2	z_2^α	z_2^β	$\omega_{12}^{\alpha\beta} / k$ [K]	ω_{12}^{DD} / k [K]	ω^{D*} / k [K]
PEG 5000	150.0	120.2	0	1.9	-473.3	120.0	-200.0
PEG 3000	90.0	72.2	0	1.9	-473.3	120.0	-200.0
PEG 300	9.0	7.4	0	1.9	-617.6	120.0	-200.0
PPG 400	12.0	9.8	0	1.4	-306.0	110.3	-75.0

k = Boltzmann constant

* = α or β

Table 2 : Parameters for LLE calculations in aqueous systems

Parameters $\omega_{12}^{\alpha\beta}$, ω_{12}^{DD} and ω^{D*} are adjustable binary parameters. Parameters r_2 , q_2 , z_2^α , and z_2^β are determined from the molecular structure of the solute. Parameters K, a and b are determined from theoretical criteria (stability criteria and scaling-law exponents) and from the coordinates of the critical point.

Solute (2)	r_2	q_2	z_2^α	z_2^β	$\omega_{12}^{\alpha\beta} / k$ [K]	ω_{12}^{DD} / k [K]	ω^{D*} / k [K]	K	a	b
Propenal	2.25	2.0	0	1.0	-756.4	197.5	-145.0	0.100	-10.0	0.36
Phenol	4.0	3.4	0.3	0.6	-661.0	115.0	-10.0	0.092	-15.0	0.36
PPG 400	12.0	9.8	0	1.4	-1033.	260.1	-120.0	0.264	-20.0	0.36
PEG 5000	150.0	120.2	0	1.9	-884.5	220.3	-103.0	0.430	-15.0	0.36
PIPAA 290000	3000.0	2400	1.1	1.1	-1354.	700.0	-137.2	1.00	-10.0	0.36

k = Boltzmann constant

* = α or β

Table A-1:

Derivation of the Maxwell condition for equilibrium between coexisting phases ' and '' for a pure fluid and for a binary mixture

Pure fluid	Binary mixture
Equilibrium conditions	
$P' = P''$	$\mu_i' = \mu_i'', \quad i = 1 \text{ or } 2$
$P = -\frac{\partial A}{\partial V}$	$\mu_i = \frac{\partial G}{\partial n_i}$
From constructing the common tangents in a plot of	
$A = f(V)$	$G = f(n_i), \quad i = 1 \text{ or } 2$
we obtain new equilibrium conditions (see Figure A-3)	
$(A + PV)' = (A + PV)''$	$(G - \mu_i n_i)' = (G - \mu_i n_i)'', \quad i = 1 \text{ or } 2$
Forming the total differentials	
$d(A + PV) = -S dT + V dP$	$d(G - \mu_2 n_2) = -S dT + V dP + n_1 d\mu_1 - \mu_2 dn_2$
intergration combined with equilibrium conditions gives	
at constant T	at constant T, P, n_2
$(A + PV)' = (A + PV)'' = \int V dP = 0$	$(G - \mu_2 n_2)' = (G - \mu_2 n_2)'' = \int n_1 d\mu_1 = 0$

Figure Captions

Figure 1: Two-dimensional representation of the oriented lattice model.

Figure 2: VLE for the system water(1)/PEG(2) at 338 K and the system water(1)/PPG(2) at 323 K.

Figure 3: LLE for the systems: a) water(1)/phenol(2), b) water(1)/propenal(2). Solid lines are calculated from the corrected model; broken lines are calculated from the uncorrected model.

Figure 4: LLE for the systems: a) water(1)/PPG 400(2), b) water(1)/PEG 5000(2), c) water(1)/PIPAA 290000(2). Solid lines are calculated from the corrected model; broken lines are calculated from the uncorrected model.

Figure 5: Swelling equilibria for the system water/PIPAA(gel). The solid line is predicted from the uncorrected model using energy parameters correlated to the uncrosslinked-PIPAA/water system (Figure 4-c). V_o is the gel volume at high temperature.

Figure A-1: Isotherms of the chemical potential of the solvent ($\Delta\mu_1 = \mu_1 - \mu_1^o$) in a solvent/gel system for a gel showing a LCST. a) 311.35 K, b) 305 K, c) 300.6 K, d) 299.4 K, e) 297.2 K and f) 295 K. The phase transition temperature is 300.6 K [curve c]. The critical temperature is 297.2 K [curve e]. The squares represent calculated equilibrium compositions of coexisting gel phases. The triangles represent calculated limits of the stable region.

Figure A-2: Phase diagram for a solvent/gel system that shows a LCST. The spinodal curve for the coexistence of two gel phases is designated by a; b is the coexistence curve for gel with pure solvent; c is the binodal curve for the coexistence of two gel phases. The squares represent calculated equilibrium compositions of coexisting gel phases. The triangles represent calculated limits of the stable region.

Figure A-3: Construction of the second step in Table A-1.

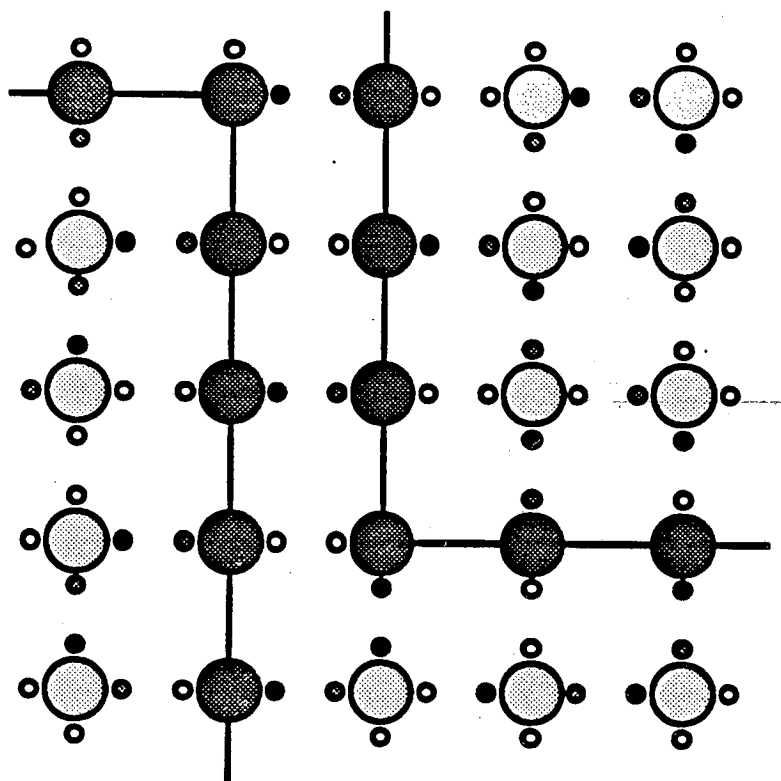
a) is a plot of Helmholtz energy versus volume in a pure fluid. The two coexisting phases ' and ''

have to fulfill the equilibrium condition $P' = P''$ or $-\left[\frac{\partial A}{\partial V}\right]' = -\left[\frac{\partial A}{\partial V}\right]''$

b) is a plot of Gibbs energy versus number of moles of component i in a mixture. The two coexist-

ing phases ' and '' have to fulfill the equilibrium condition $\mu_i' = \mu_i''$ or $\left[\frac{\partial G}{\partial n_i} \right]' = \left[\frac{\partial G}{\partial n_i} \right]''$

Figure 1



Polymer segment



Solvent molecule



hydrogen-bond donating site



hydrogen-bond accepting site



dispersion force contact site

Figure 2

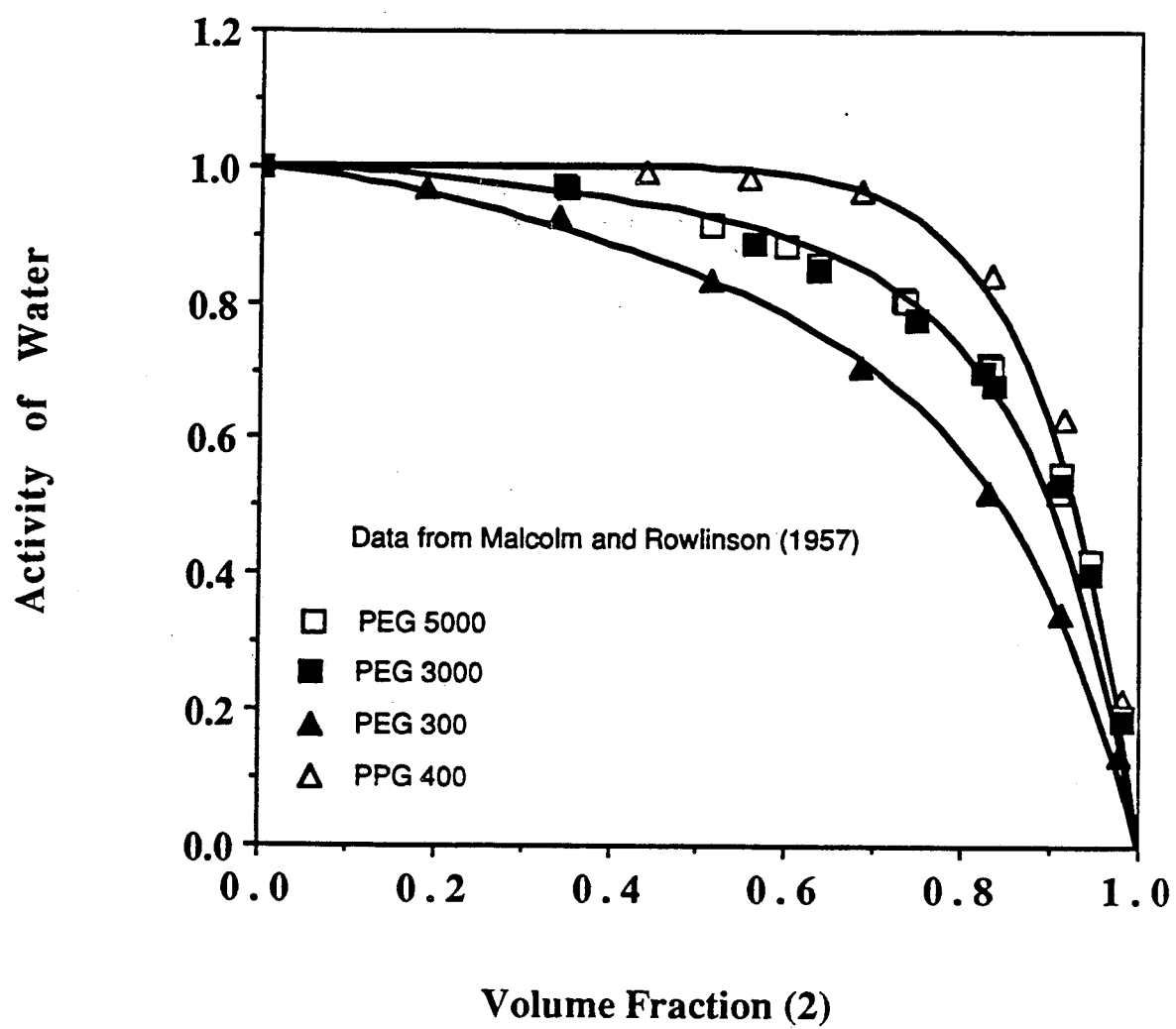


Figure 3

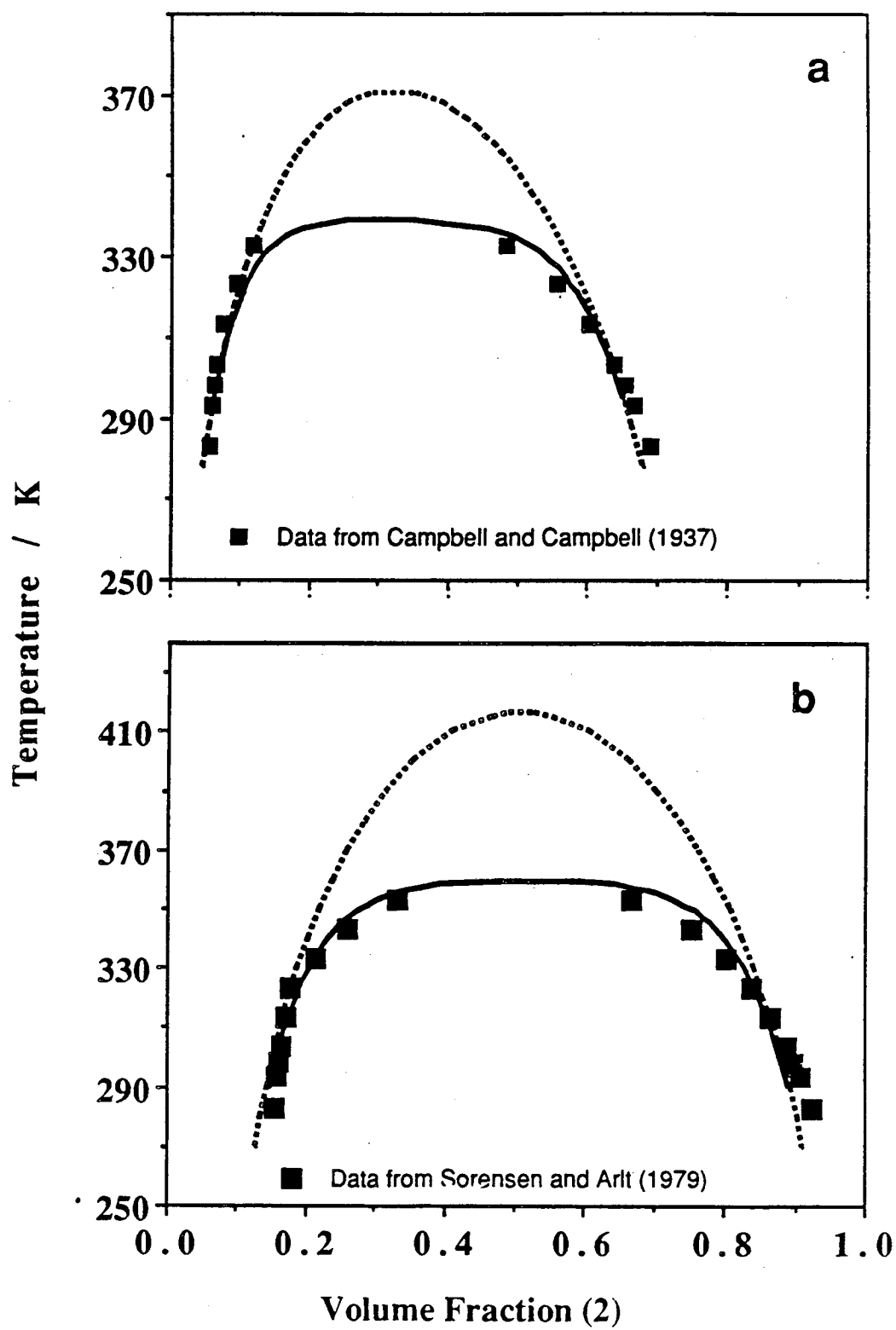


Figure 4

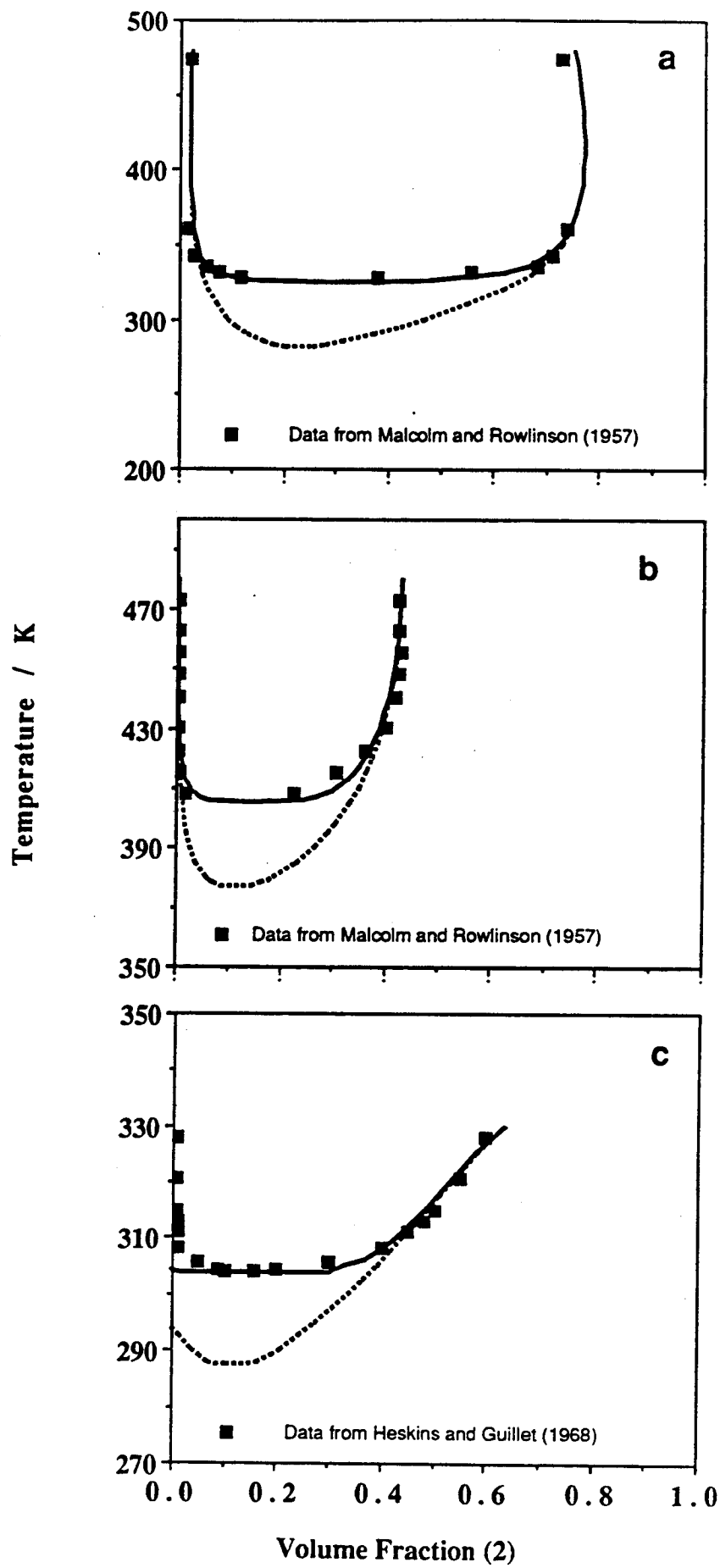


Figure 5

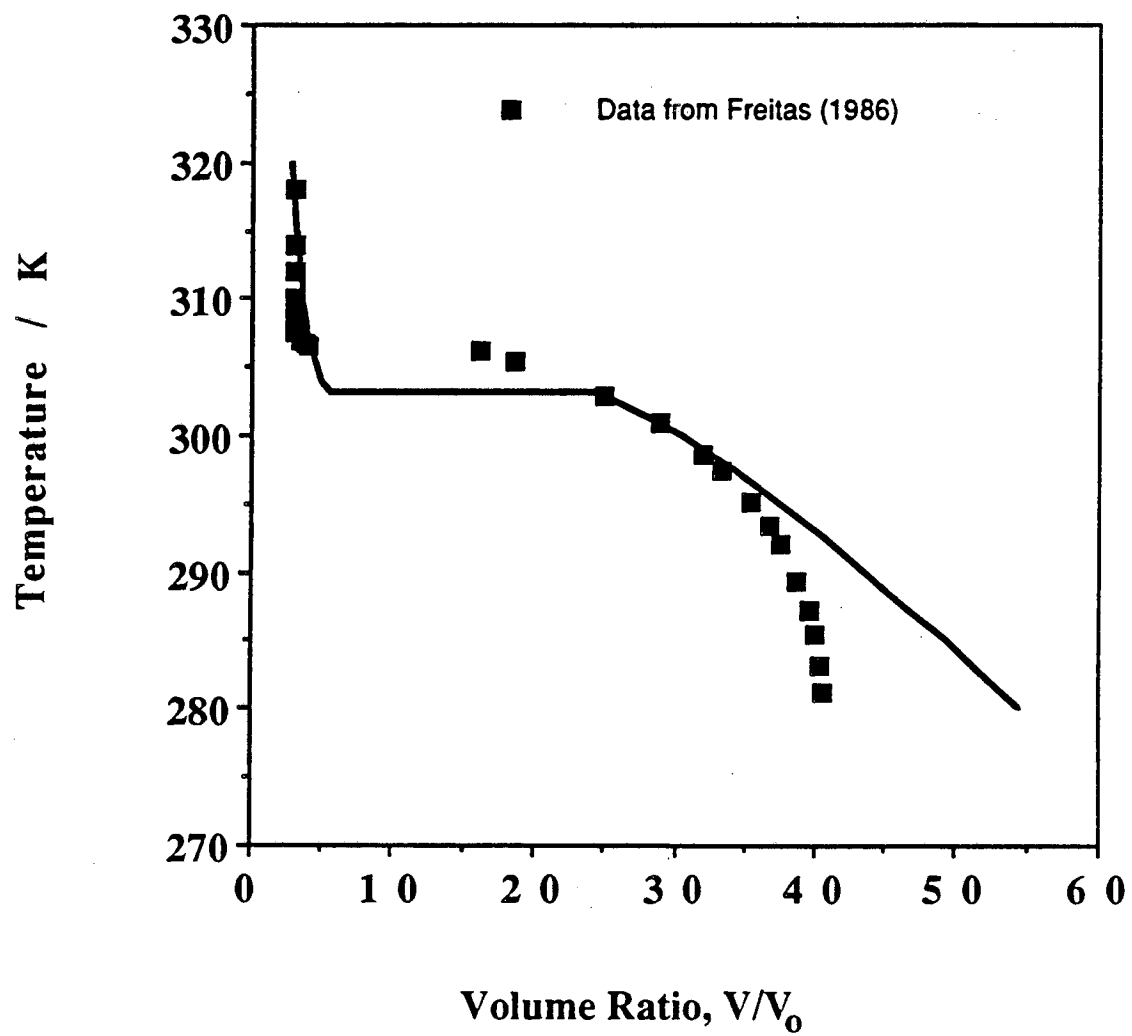


Figure A-1

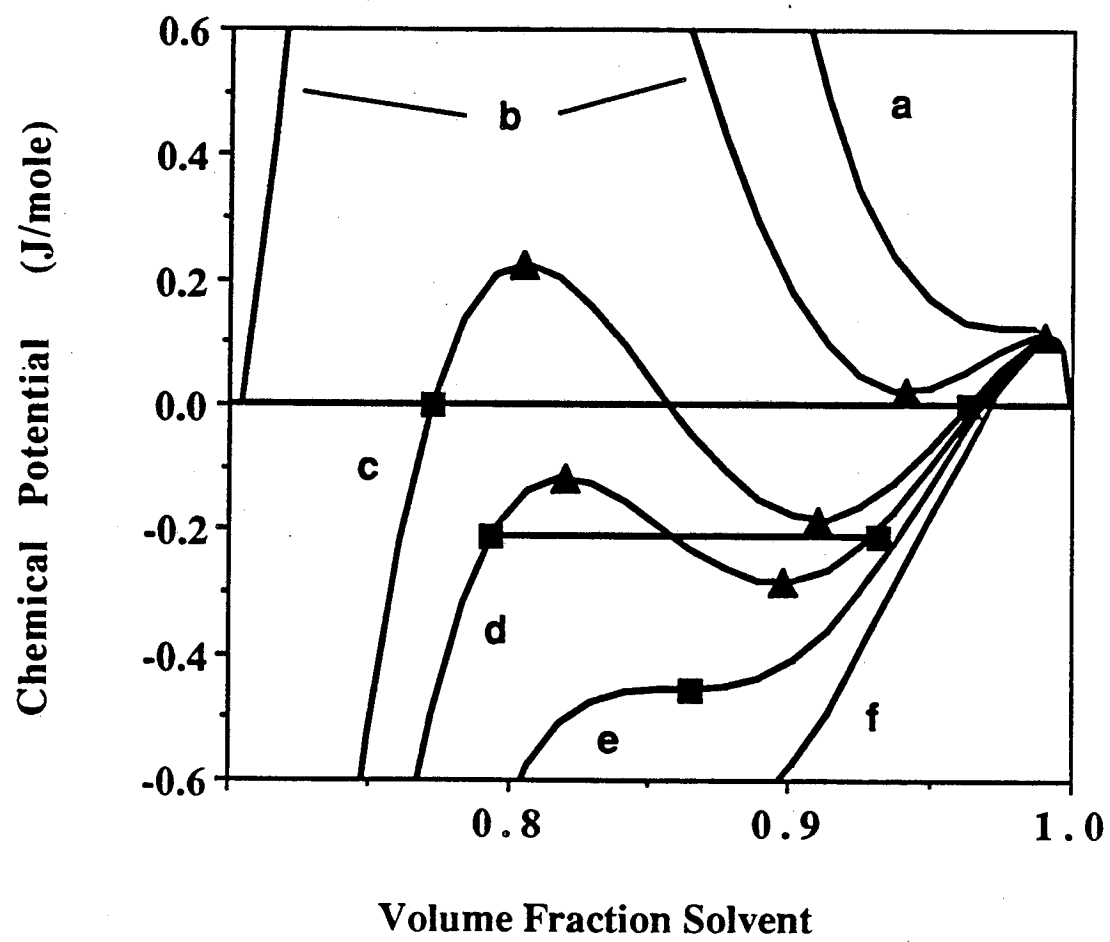


Figure A-2

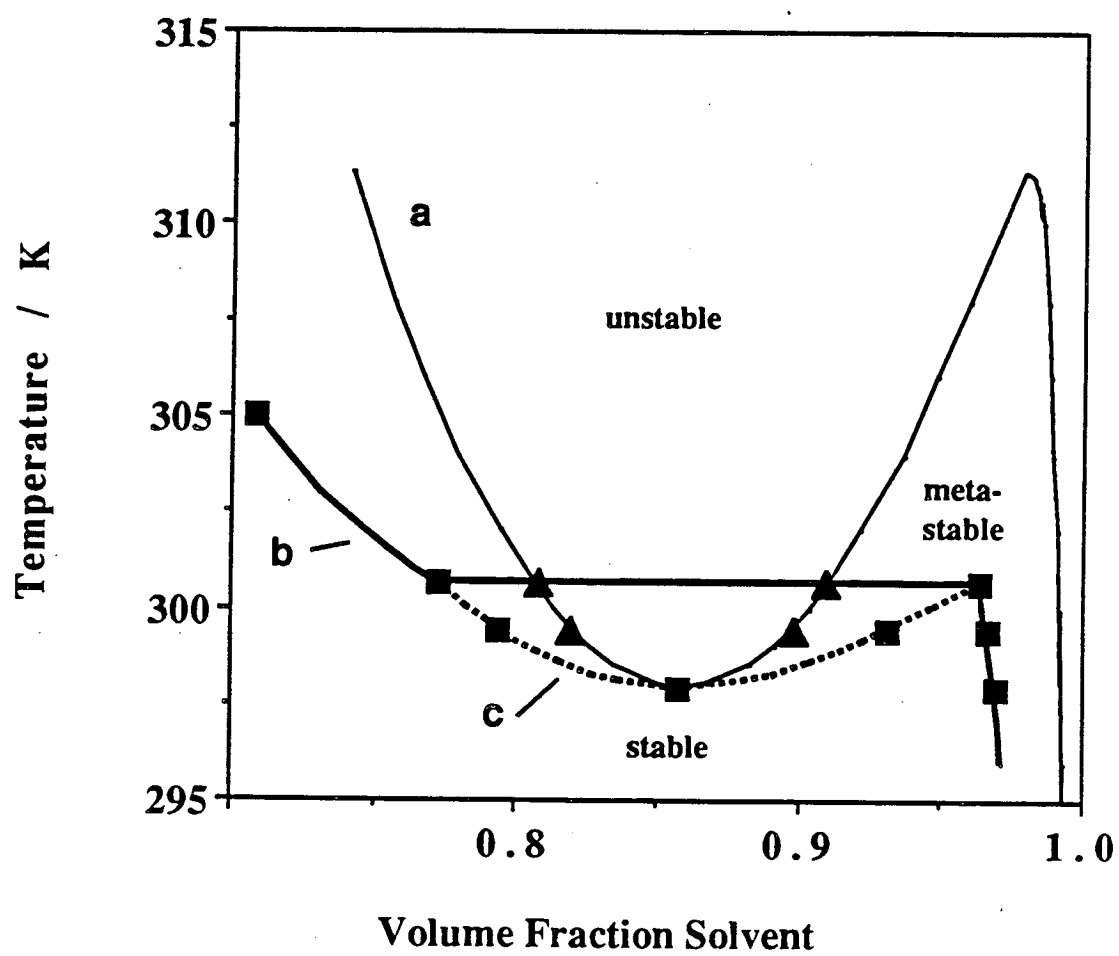
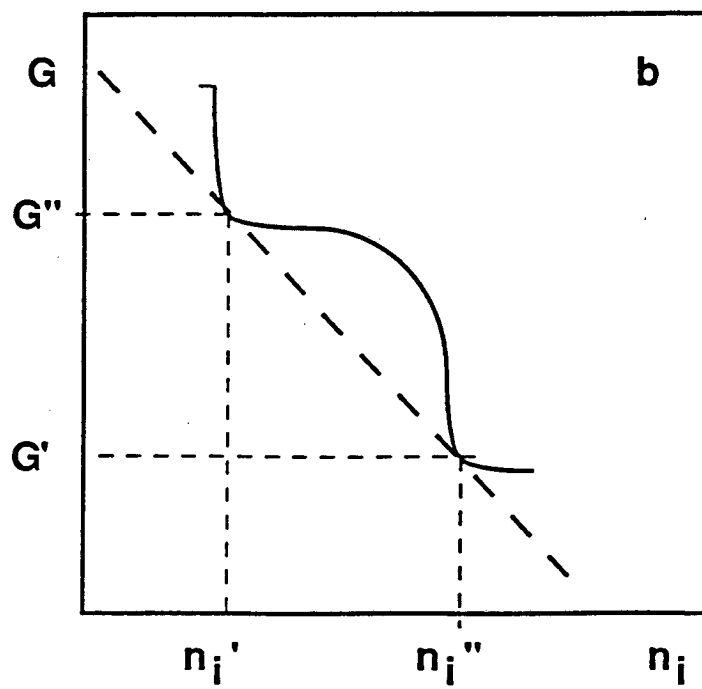
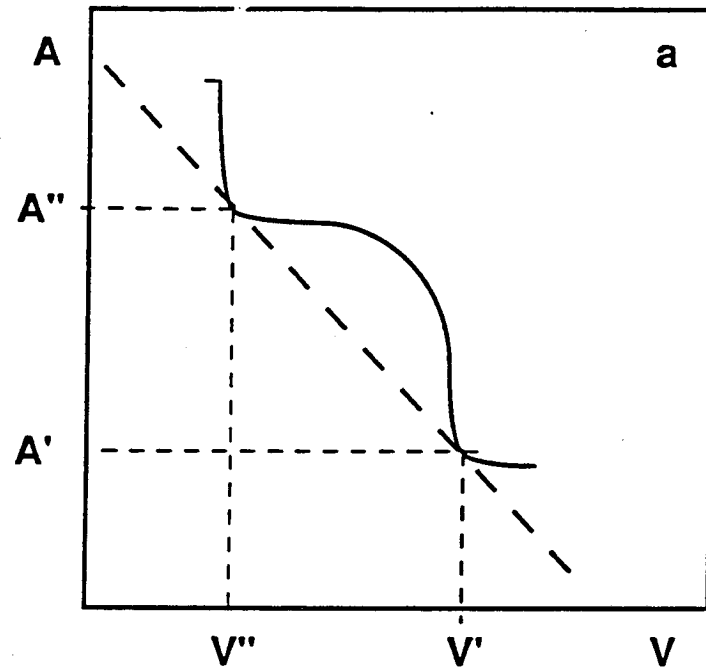


Figure A-3



LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720